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SYSTEMS AND PROCESSES FOR REMOVING ELEMENTAL SULFUR COMPOUNDS FROM DESULFURIZED FUELS

STATEMENT REGARDING FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

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FIELD OF THE INVENTION

The present invention relates generally to methods for removing sulfur from liquid fuels. More particularly, the invention includes a system and a process for removing elemental sulfur compounds from hydrocarbons including liquid fuels that have previously undergone reformat hydrodesulfurization (HDS).

BACKGROUND OF THE INVENTION

The removal of sulfur from hydrocarbon fuels reduces the sulfur dioxide emissions that result from combustion of those fuels and prevents the poisoning of expensive catalysts that utilize these fuels for other purposes. In addition, the proper operation of various technologies such as fuel cells requires the use of hydrocarbon fuels with very low sulfur concentrations. Therefore a variety of methodologies have been employed to economically and efficiently reduce sulfur concentrations in hydrocarbon fuels. Industrial hydrodesulfurization processes typically focus upon the conversion of organic sulfur to H_2S and capture and removal of hydrogen sulfide (H_2S) gas. However, these processes are still less than fully effective in removing all of the sulfur from these fuels. HDS treatment of high sulfur fuel can result in elemental sulfur compounds remaining in the fuel after one stage of treatment and in the case of very high sulfur contents in the fuel, contamination levels of up to 100 ppmw of elemental sulfur can still exist. This level of sulfur contamination makes the use of such fuels unsuitable in a steam reformer. While other approaches including a second HDS treatment or high levels of hydrogen relative to fuel may remove/reduce this sulfur contamination, the high pressure and temperature of HDS process makes this an expensive option. What is needed is a method or system for elemental sulfur removal that provides efficient enhanced sulfur removal capability and enables JP-8 and other kerosene based fuels to be sufficiently desulfurized so as to be used in steam reformers and other very low sulfur applications.

SUMMARY OF THE INVENTION

The present invention is a method for removing sulfur from hydrocarbon fuels by a stepwise process wherein hydrosulfurization reaction products are condensed at relatively low temperatures (between 50 and 200 degrees C.) to separate a liquid product from a H_2S containing gas in the vapor phase. This liquid product contains elemental sulfur which is reacted with a hydrogen containing gas in the presence of a catalyst to react the elemental sulfur with hydrogen to form H_2S which

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is then separated as a gas from the hydrocarbon liquid fuel. The remaining hydrocarbon liquid fuel is then sufficiently desulfurized so as to be suitably utilized in a steam reforming reaction. This low temperature desulfurization process provides an energy efficient way to remove sulfur to very low concentrations. This method is directly contrary to many of the methodologies in the prior art which reduce pressure on the reactant products following reaction to allow H_2S to be separated along with hydrogen gas, remove hydrogen sulfide from the hydrogen and then recompress the hydrogen in order to recycle back to the high pressure reactor. The need for this approach is to prevent an increase in HDS residual sulfur levels associated with H_2S accumulation in the recycle loop. However, this increase in residual sulfur levels is associated not with unreacted organic sulfur molecules but rather the formation of elemental sulfur molecules. The present invention, by acting contrary to the conventional wisdom in the art, obtains efficiencies and lowered sulfur levels previously unobtainable without extensive processing and cost. These systems and processes are particularly useful for desulfurization of high sulfur (e.g., ~3000 ppm) hydrocarbon fuels (e.g., JP-8).

Depending upon the needs and necessities of the user, a variety of materials may be utilized for performing the aforementioned method steps. For example, the hydrogen containing gasses utilized for reaction with the elemental sulfur may include any of a variety of materials including, but not limited to, e.g., reformat product gases (shifted or unshifted) produced using steam reforming, autothermal reforming or partial oxidation reaction; retentate gases representing the hydrogen lean stream from a hydrogen separation process including, e.g., a hydrogen permeable membrane; or any other type of hydrogen containing gas. Preferably such gasses have lowered concentrations of water to avoid water contamination of the fuel. In addition, the catalyst utilized to bind the elemental sulfur to the hydrogen to form H_2S may be any of a variety of catalysts including catalysts used to conduct the HDS reaction including NiMo and CoMo catalysts which use a molybdenum disulfide active phase as well as HDS catalysts that use a tungsten disulfide active phase, as well as a ZnO catalyst. Such catalysts may be provided as a packed bed of catalyst pellets, as catalyst coatings on random or structured packings, or any other configuration sufficient to allow the designated reactions to take place. Optimal efficiency is provided by arranging the column in a countercurrent configuration with liquid containing the elemental sulfur flowing down and hydrogen containing gas flowing up through the column. In this arrangement the hydrogen containing gas provides the dual function of enabling reaction of elemental sulfur to form H_2S and of stripping the H_2S into the gas phase to yield a desulfurized liquid product.

In order to maintain appropriate efficiencies, the separation of hydrogen containing gases from a liquid hydrocarbon takes place at a pressure drop of less than 10 psi. This reduces the cost of compressing the hydrogen containing gas for recycle to the HDS reactor. In mobile applications the ability to allow elemental sulfur formation in the HDS reaction enables the use of a smaller split stream of reformat for the HDS reaction resulting in increased efficiency. In other applications, use of a low hydrogen-containing gas:hydrocarbon ratio enables faster processing due to higher residence time in the reactor for a given hydrocarbon feed rate.

In one embodiment of the invention, optimum results were achieved when an unshifted reformat gas was introduced to the liquid hydrocarbon in the feed at a ratio at or below 1 standard liter of reformat gas per cubic centimeter (cm^3) of